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S P E C I F I C A T I O N

TO ALL WHOM IT MAY CONCERN:

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15 TETSUYA KANEKO, YOSHIKAZU BANNO and KOJIRO YOKONO,
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Mizuhiki 2-chome, Atsugi-shi, Kanagawa-ken, Japan and
2-14-308, Namiki 2-chome, Kanazawa-ku, Yokohama-shi,
Kanagawa-ken, Japan, have jointly invented a certain new
25 and useful improvement in ELECTRON-EMITTING DEVICE of
which the following is a full, clear, concise and exact
description.



- 1 -

TITLE OF THE INVENTION

Electron-emitting device

Related Application

5 *Insq* *a' >* ~~This is a continuation in part of application~~
~~Serial No. 07/218,203, filed July 13, 1988.~~

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- 1A -

BACKGROUND OF THE INVENTION

5 Field of the Invention

The present invention relates to an electron-emitting device, and a method of preparing it.

Related Background Art

Hitherto known as a device achievable of
10 emission of electrons with use of a simple structure is the cold cathode device published by M.I. Elinson et al (Radio Eng. Electron. Phys., Vol. 10, pp.1290-1296, 1965.

This utilizes the phenomenon in which electron
15 emission is caused by flowing an electric current to a thin film formed with a small area on a substrate and in parallel to the surface of the film, and is generally called a surface conduction electron-emitting device.

20 This surface conduction electron-emitting device that has been reported includes those employing a $\text{SnO}_2(\text{Sb})$ thin film developed by Elinson et al. named in the above, those employing an Au thin film (G. Dittmer, "Thin Solid Films", Vol. 9, p.317, 1972),
25 those employing an ITO thin film, (M. Hartwell and C.G. Fonstad, "IEEE Trans. ED Conf.", p.519, 1975),

1 and those employing a carbon thin film [Hisashi Araki,
et al. "SHINKU" (Vacuum), Vol. 26, No. 1, p.22, 1983].

Typical device constitution of these surface
conduction electron-emitting devices is shown in Fig.

5 38. In Fig. 38, the numerals 19 and 20 denote
electrodes for attaining electrical connection; 21, a
thin film formed using an electron-emitting material;
23, a substrate; and 22, an electron-emitting region.

In these surface conduction electron-emitting
10 devices, it has been hitherto practiced to previously
form the electron-emitting region by an energizing
heat treatment, called "forming", before effecting the
electron emission. More specifically, a voltage is
applied between the above electrode 19 and electrode
15 20 to energize the thin film 21 to bring the thin film
21 to be locally destroyed, deformed or denatured
owing to the Joule heat thereby generated, thus
forming the electron-emitting region 22 kept in a
state of electrically high resistance to obtain an
20 electron-emitting function.

What is meant by the above state of
electrically high resistance is a discontinuous state
of a film partly having cracks of 0.5 μm to 5 μm on
the thin film 21 and having the so-called island
25 structure inside the cracks. What is meant by the
island structure is the structure of a film in which

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1 fine particles generally having a diameter of several
ten angstroms to several micrometers are present on
the substrate, and the respective fine particles are
spatially discontinuous and electrically continuous.

5 Hitherto, in the surface conduction
electron-emitting devices, a voltage is applied to the
above high-resistance discontinuous film by the
electrodes 19 and 20 to flow an electric current to
the surface of the device, so that the electrons are
10 emitted from the above fine particles.

 However, the forming according to the
conventional energizing heat treatment as mentioned
above have involved the problems as follows:

(1) In carrying out the energizing heating, it
15 sometimes occurs that the thin film is peeled because
of the difference in coefficient of thermal expansion
between the substrate and the thin film. This
provides limitations in upper limit of heating
temperature, materials for the substrate, and
20 combination by selection of materials for the thin
film.

(2) In carrying out the energizing heating, the
substrate also is locally heated, therefore sometimes
resulting in occurrence of fatal cracking therein.

25 (3) Degree of the changes of a film owing to the
energizing heating, as exemplified by the degree of

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1 local destruction, deformation or denaturing, tends to
become irregular among a plurality of devices formed
in the same substrate, and also the site at which
changes may occur tends to be not fixed.

5 For this reason, when functioned as an
electron-emitting device, irregularity in the shape of
beams of emitted electrons has been seen for each
device.

(4) A relatively large electric power is required
10 until the forming is completed. For this reason, an
electric source of large capacity is required when a
number of devices are formed on the same substrate and
the forming is carried out simultaneously.

(5) A relatively long period of time is required
15 for conventional forming processes that start with the
energizing heating and end with cooling. For this
reason, *an excessively* ~~a greatly~~ long time is required for carrying
out the forming of a number of devices.

Because of the problems as set out above, the
20 surface conduction electron-emitting devices have not
been positively applied in industrial fields,
notwithstanding their advantages that the device has
simple construction.

25 SUMMARY OF THE INVENTION

The present invention was made to eliminate

1 the disadvantages in the prior art as discussed above,
and an object thereof is to provide an electron-
emitting device that can have, without applying the
treatment called forming, a quality more than equal to
5 that of electron-emitting devices obtained by the
forming, and has a novel structure suffering less
irregularity of characteristics, and a method for
preparing it.

More specifically, the present invention
10 firstly provides a means for preparing the device by
controlling the above-mentioned shape and width of
cracks without use of the forming means, and with
ease, and provides an electron-emitting device with
regular characteristics, prepared by the method using
15 the means.

It secondly provides a means for making
uniform the structure and size corresponding to the
island structure in the cracks mentioned above, and
provides an electron-emitting device having regular
20 characteristics by using the means.

A further object of the present invention is
to provide an electron-emitting device capable of
controlling the above characteristics and also capable
of better controlling the position of the electron-
25 emitting region, and a method for preparing such a
device.

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1 A still further object of the present
invention is to provide an electric current emitting
device that not only can solve the problems previously
mentioned, but also can make lower the voltage to be
5 applied to electrodes and achieve improvement in the
density of an emitted electric current.

 According to an aspect of the present
invention, there is provided an electron-emitting
device comprising a laminate comprising an insulating
10 layer held between a pair of electrodes opposing each
other, wherein an electron-emitting region insulated
from said electrodes is formed at a side end surface
of the insulating layer formed at the part at which
the electrodes oppose each other, and electrons are
15 emitted from said electron-emitting region by applying
a voltage between said electrodes.

 According to another aspect of the present
invention, there is provided an electron-emitting
device comprising a device structure in which an
20 insulating layer is formed between opposing electrodes
, and fine particles are arranged inside the layer of
said insulating layer in a dispersed state.

 According to a further aspect of the present
invention, there is provided an electron-emitting
25 device comprising the device structure that a
semiconductor layer is formed between opposing

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1 electrodes , and fine particles are arranged inside
the layer, or on the layer, of said semiconductor
layer in a dispersed state.

Ins. B1
Ins. B2
5 BRIEF DESCRIPTION OF THE DRAWINGS

B2
~~Fig. 1 to Fig. 7 are cross sections
illustrating vertical type electron-emitting devices
of the present invention;~~

Fig. 8 is a perspective view illustrating an
10 electron-emitting device of the present invention
having an insulating layer comprising fine particles
arranged in a dispersed state;

Fig. 9 and Fig. 10 are cross sections along
the line A to B in Fig. 8;

Ins. B3
15 ~~Fig. 11 and Fig. 14 are views explanatory of
the preparation processes of electron-emitting devices
of the present invention;~~

Fig. 12, Fig. 13, Fig. 15 and Fig. 16
diagrammatically illustrate electron-emitting devices
20 according to other embodiments of specific structures
of the present invention;

Ins. B4
B4
25 ~~Fig. 17 to Fig. 27 diagrammatically illustrate
electron-emitting devices of the present invention
having a semiconductor layer comprising fine particles
arranged in a dispersed state;~~

~~Fig. 28 to Fig. 36 diagrammatically illustrate~~

Ins. 65 1 ~~electron-emitting devices according to other~~
65 ~~embodiments of specific structures of the present~~
~~invention;~~

18 *Figs. 37(a) and 37(b)*

18 ~~Fig. 37~~ diagrammatically illustrates an
5 electron-emitting device comprising two kinds of fine
particles arranged in a dispersed state; and

Fig. 38 is a view illustrating a conventional
electron-emitting device

Ins. 66 10 DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

More specifically, the present invention is an
electron-emitting device comprising a laminate
comprising an insulating layer disposed between a pair
of opposing electrodes, wherein an electron-emitting
15 region insulated from the electrodes is provided at a
side end surface of the insulating layer formed at the
part at which the electrodes oppose each other, and
electrons are emitted from the electron-emitting
region by applying voltage between the electrodes.

20 Fig. 1 diagrammatically illustrates a first
embodiment of the electron-emitting device of the
present invention. In the figure, the numerals 1 and
2 denote electrodes for obtaining electrical
connection; 3, an electron-emitting region; 4, a
25 substrate; and 5, an insulating layer.

In Fig. 1, the electron-emitting device of the

1 present invention comprises a laminate comprising the
insulating layer 5 disposed between a pair of the
electrodes 1 and 2 opposing each other at their end
portions, wherein the electron-emitting region 3
5 insulated from the electrodes is provided at a side
end surface of the insulating layer 5 formed at the
opposing part at which the electrodes 1 and 2 oppose
each other, and electrons are emitted from the
electron-emitting region 3 by applying voltage between
10 the electrodes 1 and 2.

In the above electron-emitting device, the one
corresponding to the narrow crack in the prior art can
depend on the film thickness of the insulating layer
5. More specifically, as illustrated in Fig. 1,
15 taking the structure that a pair of the electrodes are
formed above and beneath the insulating layer with
respect to the direction of the lamination in which
the insulating layer having the electron-emitting
region is laminated to the substrate (hereinafter
20 referred to as "vertical type structure") can make
small the thickness of the insulating layer on which
the spacing between electrodes depend.

The electron-emitting device having the
vertical type structure has a quality more than equal
25 to that of conventional ones without taking the
forming means, and can give a more improved electron-

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1 emitting device that can make uniform the shape and width of the electron-emitting region.

In Fig. 1, the insulating layer 5 may have a thickness of from several angstroms to several
5 microns, for example, from 10 angstroms to 10 microns, preferably from 10 to 1 μm .

The insulating layer 5 is comprised of SiO_2 , MgO , TiO_2 , Ta_2O_5 , Al_2O_3 or the like, a laminated material of any of these, or a mixture of any of
10 these, which is formed by vacuum deposition or coating. Alternatively, when the electrode 1 is comprised of a metal such as Al and Ta, the insulating layer 5 may comprise an anodic oxidation film anodized by electrolysis.

15 The substrate 4 is formed with glass, ceramics or the like, and the electrodes 1 and 2 are formed with Au, Ag, Cu, Mo, Cr, Ni, Al, Ta, Pd, W or the like, or an alloy of any of these, or carbon, etc.

The electrodes 1 and 2 may have a thickness of
20 from several hundred angstroms to several μm , preferably from 0.01 to 2 μm in the case of the vertical type. Formation methods include vacuum deposition, photolithography, and printing.

An outline of the method of preparing the
25 electron-emitting device according to the present invention can be specifically described based on Fig.

1 1 as follows:

The electrode 1 is vapor deposited on the substrate 4, and then subjected to patterning to give a desired shape as exemplified by a stripe.

5 Thereafter, the insulating layer 5 is formed by means of vacuum deposition, coating or the like. Thickness of the insulating layer depends on the dielectric strength depending on materials for the insulating layer, and the threshold voltage at which emission of
10 electrons begins by the voltage applied between the electrodes 1 and 2. Usually, to set the threshold voltage to from 10 to 20 V, this film thickness must be 1 microns or less. After formation of the insulating layer 5, the electrode 2 is formed by
15 conventional vacuum deposition, printing, coating or the like process, and then the electrode 2 and the insulating layer 5 are so subjected to patterning along the pattern of the electrode 1 that they may partly overlap with the electrode 1 in the same
20 pattern. (See Fig. 1.) In that occasion, the electron-emitting region 3 may be obtained by disposing an electron-emitting layer 3a between the insulating layers 5a and 5b according to the manner as described later, or may be obtained by disposing electron-
25 emitting bodies 3b at the side face of the insulating layer 5.

1 Good results can also be exhibited not only by
taking the structure in which the electrodes 1 and 2
overlap as shown in Fig. 1, but also by an electron-
emitting device comprising the electron-emitting
5 region 3 disposed at a side end surface defined
between a pair of electrodes 1 and 2 that oppose at
their end portions but have no overlap as shown in
Fig. 2.

 The electron-emitting region 3 is formed by
10 disposing an electron-emitting layer 3a in the
insulating layer 5 comprised of a material readily
capable of field emission of electrons, a material
readily capable of secondary electron emission, or a
material readily capable of emitting electrons by
15 electron bombardment and having strong thermal
resistance and corrosion resistance, as exemplified by
metals such as W, Ti, Au, Ag, Cu, Cr, Al and Pt,
oxides such as SnO_2 , In_2O_3 , BaO and MgO, or carbon or
a mixture of any of the above, each having a low work
20 function and high thermal resistance, utilizing vacuum
deposition, coating, sputtering deposition, dipping,
or the like process.

 Alternatively, it may comprise a thin coating
comprising superfine particle powder of metals as
25 exemplified by Au, Ag, Cu, Cr and Al, or can be also
formed by arranging electron-emitting bodies 3b at the

1 side face of the insulating layer 5 comprising a thin
coating of the material as described for the above
electron-emitting layer 3a. (Utilizable coating
methods include spreading, all sorts of vacuum
5 deposition, and dipping.)

Electrode spacing 6 in Fig. 1 and Fig. 2
somewhat differs, but in approximation may desirably
be formed in from several ten angstroms to several μm .
preferably from several ten angstroms to 2 μm , and
10 more preferably from 10 angstroms to 1 μm .

An outline of a method for preparing the
electron-emitting device illustrated in Fig. 2 will be
described below.

An insulating layer 5 is formed on a substrate
15 4, and a stepped portion is formed by patterning.

Thereafter the electrodes 1 and 2 are simultaneously
formed into films so that the stepped portion may not
be covered by the electrodes, thus forming the
electrode spacing 6. Accordingly, the electrode
20 spacing 6 depends on thickness of the electrode formed
at the stepped portion set with the film thickness of
the insulating layer 5. The film formation of this
electrode is carried out usually by using vacuum film
formation or a similar process, so that it is possible
25 to control the film thickness in high precision.

Thus, for the electrode spacing 6, small spacing of

1 several ten angstroms can be readily obtained in high
precision.

The stepped portion at which the electrode
spacing 6 is formed can also be obtained by pattern
5 etching of the substrate 4 itself, without using the
insulating layer 5. There is also available a method
in which the electrodes 1 and 2 are formed on this
stepped portion to obtain an electron-emitting device.
(See Fig. 7.)

10 Taking the structure that a pair of the
electrodes opposing each other have no mutual overlap
as illustrated in Fig. 2 can bring about a more
superior electron-emitting device suffering less
increase in driving power consumption that may be
15 otherwise caused by increase in the electrical
capacity at the part at which the electrodes overlap,
less delay of driving electric signals, and less
influence by dielectric strength or pinholes of the
insulating layer.

20 On the other hand, the electron-emitting
device having the structure as shown in Fig. 7 makes
it unnecessary for the electrodes to be held by the
insulating layer, and makes it possible also to obtain
the spacing of the opposing electrodes by utilizing
25 the stepped portion, so that if, for example, the
electrodes-supporting substrate itself is etched to

1 provide the stepped portion, there is given an
electron-emitting device that can be obtained without
formation of any insulating layer, making simple its
preparation processes.

5 The electron-emitting device of the present
invention may further have the structure as shown in
Fig. 4.

 In Fig. 4, the numerals 1 to 5 denotes the
same as those in Fig. 3. In the present figure, the
10 numeral 8 denotes an intermediate layer, which is
disposed between the insulating layer 5 and the
electrode 2 to constitute a multi-layer electrode.
The intermediate layer 8 plays a role to bring about
the effect of preventing sputtering damage caused by
15 electrons or ions in the electrode 2, or the effect of
bringing electrons to more readily emit. As the
intermediate layer 8, high-melting materials as
exemplified by W, LaB_6 , carbon, TiC and TaC may be
used to make small the sputtering damage, and
20 materials having a low work function as exemplified by
 SnO_2 , In_2O_3 , LaB_6 , BaO, CS and CSO may be used to
achieve improvement in electron emission efficiency.

 There may be also used a laminate, or a
mixture, comprising these both materials. Of course,
25 similar effect can be obtained also when the
intermediate layer 8 is provided on the electrode 1 to

1 give a multi-layer electrode. Further, when both the
electrodes are made to comprise the multi-layer
electrode, suitable materials for the intermediate
layer 8 can be selected for each electrode. Also, a
5 laminate comprising an insulating layer 5a, an
electron-emitting layer 3a and an insulating layer 5b
may be made to comprise a multi-layer laminate
constituted of, for example, an insulating layer 5a,
an electron-emitting layer 3a, an insulating layer 5b,
10 an electron-emitting layer 3a, an insulating layer 5a,
and an electron-emitting layer 3a. At least one layer
of the multi-layer electrodes, as exemplified by the
electrode 2 in Fig. 4, may further preferably be
comprised of a material having a high electrical
15 conductivity. This is because the materials for the
intermediate layer 8 are materials having relatively
low electrical conductivity as for electrode wiring
materials.

An excessively high wiring resistance of a
20 device may cause an increase in the power consumption
or a delay in the driving signals, resulting in
undesirableness in driving the device. For this
reason, the materials having high electrical
conductivity is used in the electrode 2 to keep to a
25 low level the wiring resistance of the whole multi-
layer electrode. Usable as the materials having high

1 electrical conductivity are Ag, Al, Cu, Cr, Ni, Mo,
Ta, W, etc.

In Fig. 4, when the electron-emitting layer 3a
comprises the material suffering less sputtering
5 damage or having a low work function, the intermediate
layer 8, or the electrode 1 and the intermediate layer
8, may be formed with use of the same materials as in
the electron-emitting layer 3a.

The present invention further provides an
10 electron-emitting device having a device structure
wherein an insulating layer is formed between
electrodes opposing each other, and fine particles are
contained in said insulating layer and at the same
time arranged in a dispersed state.

15 Taking the above described device structure of
the present invention not only can solve the problems
in the prior art previously discussed, but also can
provide an electron-emitting device capable of
obtaining an emitted electric current of high density
20 by using a low electric power and also capable of
controlling the island spacing, island size of the
islands previously mentioned. This electron-emitting
device will be described below with reference to the
drawings.

25 In Fig. 8, provided on a substrate 4 such as
glass and ceramics is an insulating layer 11, and

1 further thereon electrodes 1 and 2 comprised of low-
resistance materials for use in voltage application
are provided giving minute spacing to form a
discontinuous electron-emitting region 10 comprising
5 fine particles 9 dispersed between them. Though not
shown in the drawing, a space is taken at an upper
area of the electron-emitting region to provide there
a lead-out electrode for leading out emitted
electrons. Application of voltage between the
10 electrodes 1 and 2 in vacuo (this voltage is assumed
as V_f) brings about flow of electricity between the
electrodes (I_f) to apply voltage using the lead-out
electrode as the anode, so that electrons are emitted
from the electron-emitting region in the direction
15 substantially vertical to the paper surface in the
drawing. (The electric current for this electron
emission is assumed as I_e .)

Fig. 9 and Fig. 10 diagrammatically illustrate
cross sections in the A-B direction in Fig. 8. In the
20 present figures, the fine particles on the substrate 4
may preferably have a particle diameter of from
several ten angstroms to several μm , and the spacing
between respective fine particles may further
preferably be formed in the range of from several ten
25 angstroms to several μm .

Materials for the fine particles used in the

1 present invention may cover a very wide range, and
almost all of conductive materials including usual
metals, semimetals and semiconductors. Particularly
suitable are usual cathode materials having properties
5 such as low work function, a high melting point and
low vapor pressure, thin film materials capable of
forming the surface conduction electron-emitting
device by the conventional forming treatment, and
materials having a large coefficient of secondary
10 electron emission.

Appropriate materials may be selected from
such materials according to purposes and used as the
fine particles, so that a desired electron-emitting
device can be formed.

15 Specifically, they may include, for example,
borides such as LaB_6 , CeB_6 , YB_4 , and GdB_4 , carbides
such as TiC , ZrC , HfC , TaC , SiC and WC , nitrides such
as TiN , ZrN and HfN , metals such as Nb, Mo, Rh, Hf,
Ta, W, Re, Ir, Pt, Ti, Au, Ag, Cu, Cr, Al, Co, Ni, Fe,
20 Pb, Pd, Cs and Ba, metal oxides such as In_2O_3 , SnO_2
and Sb_2O_3 , semiconductors such as Si and Ge, carbon,
and AgMg. The present invention is by no means
limited by the above materials. Moreover, in the
present invention, it may also be practiced to select
25 different materials among the above materials and
disperse fine particles of two or more kinds of

1 different materials.

A method for preparing the device illustrated in Fig. 8 will be described below.

Fig. 11 (1) to (5) illustrate cross sections of a device for each preparation step.

(1) The surface of a substrate 4 comprised of glass or ceramics is degreased and cleaned.

(2) An insulating layer 11 comprised of low-melting point glass is formed into a film on the surface of the substrate 4 according to liquid-coating baking, printing baking, vacuum deposition, or the like process. Desirable as materials for the low melting point glass are those having a softening point temperature lower than the distortion point temperature of the substrate and at the same time having a coefficient of thermal expansion close to that of the substrate. In general, a lead oxide type low melting glass has a softening point of about 400°C and also has a coefficient of thermal expansion close to the coefficient of thermal expansion of a soda lime glass substrate generally used. The insulating layer 11 may desirably be formed to have a thickness in the range of from several ten angstroms to several ten μm in approximation.

(3) On the insulating layer obtained in (2), electrodes 1 and 2 are formed according to vacuum

1 deposition, photolithoetching, lifting-off, printing,
or the like process.

Usable as electrode materials are the same
materials as those described in relation to Fig. 1,
5 i.e. Au, Ag, Cu, Mo, Cr, Ni, Al, Ta, Pd and W, or an
alloy of any of these or carbon, etc., and the
electrodes 1 and 2 may also suitably have a thickness
of from several hundred angstroms to several μm ,
preferably from 0.01 to 2 μm .

10 As to the dimension of electrode spacing L,
the electrodes may suitably oppose each other with a
space of from several hundred angstroms to several ten
 μm , and spacing width W may suitably be approximately
from several μm to several mm. However, they are by
15 no means limited to these dimensions.

(4) Next, the fine particles 9 are coated on the
electrode gap region obtained in (3). A dispersion of
fine particles are used in the coating. Fine
particles and an additive to promote dispersion of the
20 fine particles are added in an organic solvent
comprised of butyl acetate, alcohol or the like,
followed by stirring or the like to prepare the
dispersion of fine particles. This fine particle
dispersion is coated on the surface of a specimen
25 according to dipping, spin coating or the like
process, and then calcination is carried out for about

1 10 minutes at a temperature at which the solvent or
the like may be evaporated, for example, at 250°C.
Thus the fine particles are arranged on the surface of
the insulating layer 11 in the electrode spacing L.
5 Of course, the fine particles 9 are arranged on the
whole surface of the specimen, but no difficulty is
brought about as there is applied substantially no
voltage to the fine particles 9 outside the electrode
spacing L when electrons are emitted. This is
10 accordingly not shown in the drawing. Arrangement
density of the fine particles 9 may vary depending on
the coating conditions and how to prepare the fine
particle dispersion, and the amount of electric
currents flowing to the electrode spacing L may also
15 vary in accordance with this. In addition to the
above formation by coating, also available as a method
for dispersing the fine particles 9 to the electrode
gap region obtained in (3) is, for example, a method
in which a solution of an organic compound is coated
20 on the substrate followed by thermal decomposition to
form metal particles. In regard to materials feasible
for vacuum deposition, the fine particles can be also
formed by control of vacuum deposition conditions such
as substrate temperature or by a means like vacuum
25 deposition such as masked vacuum deposition.

(5) After this, the specimen obtained through the

1 steps up to (4) is heated to a temperature higher than
the softening point of the low-melting glass
constituting the insulating layer 11, for example, to
450°C if it is the lead oxide type low-melting glass,
5 to carry out baking for about 20 minutes. By this
procedure, the fine particles 9 arranged on the
insulating layer 11 comprised of the low ^{melting} ~~meting~~ glass
penetrate into the low-melting glass, resulting in
being included (or enclosed) into the insulating layer
10 11, or included to the extent that at least part of a
particle is exposed from the insulating layer 11, and
then fixed there.

Whether the fine particles 9 are brought into
the state that all of them are included into the
15 insulating layer 11 or the state that only part of a
particle penetrates into the insulating layer 11 in
the state that the surface remains exposed, may be
adjusted by selecting the baking temperature in the
step (5).

20 The higher the baking temperature is, the more
readily the fine particles 9 are penetrated deeply
into the insulating layer 11, and are included and
fixed. A lower baking temperature may make it
difficult for the fine particles 9 to penetrate into
25 the insulating layer 11, and tend to make them fixed
in the exposed form.

1 Some of the materials such as Pd listed in the
above embodiment may be covered on their surfaces with
oxide films as a result of heating in the above step
(5), resulting in decrease in the amount of the
5 electric current flowing to the electrode spacing L.
Therefore, a step of pickling to remove the oxide film
may be introduced if necessary.

 In the present invention, the device may also
be formed by bringing the fine particles 9 to be
10 completely included into the insulating layer 11 and
thereafter carrying out etching to bring part of each
particle to be exposed.

 Not only the device prepared according to the
above preparation steps, having the structure as
15 illustrated in Fig. 11, but also the devices having
the structure illustrated in Fig. 12 and Fig. 13(a)
and (b) can also exhibit good results.

 Preparation processes in Fig. 12 will be
described.

20 Electrodes 1 and 2 are formed on a substrate
4, on which a fine particle dispersion or a dispersion
prepared by mixing low-melting frit glass into an
organic metal compound solution is coated in the
vicinity of the electrode spacing region L, followed
25 by baking at a temperature higher than the softening
point of the low-melting frit glass crystalline

1 melting point to bring the fine particles to be
included into an insulating layer 11 comprised of the
low-melting glass, or bring at least part thereof to
be exposed, and then fixed. Here, the baking
5 temperature set to a higher degree (as exemplified by
650°C enables the smoothing of the insulating layer 11
to make a continuous film.

In the figure, the insulating layer 11 may
preferably be formed to have a film thickness of from
10 several ten angstroms to several μm in approximation.

Here, a liquid coating insulating layer (as
exemplified by Tokyo Ohka OCD, a SiO_2 insulating
layer) may be used in place of the low-melting frit
glass.

15 In the instance where the liquid coating
insulating layer is used, it is also possible to
obtain the electron-emitting device of the present
invention in the following manner: First, the
insulating layer 11 containing the fine particles 9 is
20 built up on the substrate 4 according to liquid
coating. Namely, it can be obtained by coating the
fine particles mixed and dispersed in a liquid coating
preparation, on a substrate by spin coating, dip
coating or the like.

25 Next, electrodes are formed on the insulating
layer 11 according to the above processes such as

1. vacuum deposition to make up an electron emission device.

Taking said process, the fine particles are coated on the substrate in the state that they are
5 mixed and dispersed in the liquid coating preparation or the like for obtaining the insulating layer, and therefore, even after the coating and baking, they remain dispersed in a good state in the film formed by coating the liquid coating preparation for obtaining
10 the insulating layer. Accordingly, the fine particles suffer less agglomeration, and can be uniformly dispersed in the insulating layer obtained by the liquid coating preparation.

Also, since in the present structure the
15 insulating layer containing fine particles is first formed on the substrate, the substrate surface before formation of the insulating layer is usually a uniform surface without any particular pattern or roughness. Accordingly, since the insulating layer containing the
20 fine particles in its uniform surface is formed by coating and baking, there is no non-uniformity in the film thickness or fine particle dispersion owing to coating unevenness at the part of the pattern or roughness, so that a support layer in which the fine
25 particles are dispersed can be uniformly formed on the substrate surface. Obtaining the insulating layer

1 that is uniform like this can make small the
irregularity or the like in device characteristics
when a number of electron-emitting devices are
provided on the same substrate.

5 Moreover, although in the present structure an
in-air heating step at about 400°C or more becomes
necessary, for example, when the oxide type insulating
layer is formed using the liquid coating preparation,
the electrodes themselves do not pass through the
10 heating step because the insulating layer formation
heating is carried out before formation of the
electrodes. Therefore, no account is required to be
taken for the thermal oxidation of electrodes or
thermal diffusion with respect to the insulating
15 layer, thus enabling expansion of the range of
selection for electrode materials.

 Accordingly, the materials may be
appropriately selected depending on the conditions
such as dielectric strength, thermal resistance,
20 workability, oxidation resistance, life, specific
resistance, and amount of electric current that can be
taken out. The materials for the insulating layer may
include, as previously described, SiO_2 , MgO , TiO_2 ,
 Ta_2O_5 and Al_2O_3 , or a laminate or mixture of any of
25 these. The film thickness may be from about 10
angstroms to several μm or so, which is the thickness

1 necessary for the fine particles 9 to be dispersed and
fixed.

The electron-emitting device may also have the
structure as illustrated in Fig. 13.

5 In the electron-emitting device illustrated in
Fig. 13, a fine particle dispersion prepared by mixing
the low-melting frit glass for the insulating layer 11
is coated (here, carried out in the same manner as
described in relation to Fig. 12), and thereafter the
10 insulating layer 11 is formed into a discontinuous
island-shaped film by setting the baking temperature
to somewhat lower degree (for example, about 500°C).

In the electron-emitting device illustrated in
Fig. 13, the insulating layer 11 does not entirely
15 cover the electrode spacing L as so illustrated in the
figure, so that it takes the form that the electrode
ends of the electrodes 1 and 2, on the side of the
electrode spacing L, i.e., the part at which a highest
electric field is generated, is connected with the
20 surface and inside of the insulating layer 11. For
this reason, the degree of freedom of the electric
current flow path becomes greater, so that the amount
of electric current flowing between the electrodes can
be more increased than the device of Fig. 12.

25 Both the electron-emitting device of Fig. 12
and the electron-emitting device of Fig. 13, in which

1 the insulating layer and the fine particles can be
formed simultaneously, have the advantage that the
preparation steps can be simplified.

The electron-emitting device of the present
5 invention may further comprise a device having the
structure as illustrated in Fig. 14(5).

In Fig. 14, the numeral 4 denotes a substrate;
1 and 2, electrodes; 9, fine particles; and 11, an
insulating layer.

10 Fig. 14 (1) to (5) illustrate cross sections
of a device for each preparation step.

1) The surface of the substrate 4 is degreased
and cleaned.

2) The electrodes 1 and 2 are formed in the same
15 manner as in (3) in Fig. 11.

3) The fine particles are dispersed in the same
manner as in step (4) in Fig. 11.

4) The insulating layer 11 is formed by a method
of EB vacuum deposition, sputtering, or vacuum
20 deposition such as plasma CVD, heat CVD or the like
process. Usable as materials for the insulating layer
11 are oxides such as SiO_2 and Al_2O_3 , nitrides such as
 Si_3N_4 , carbides such as SiC and TiC , as well as glass
obtained by vacuum deposition or solution-coated
25 baking, and insulating layers comprising organic
polymers such as polyimides. Also, the layer 11 may

1 desirably have a film thickness of from several 10
angstroms to several μm . Here, in general, the
insulating layer 11 is deposited also on the surface
of fine particles 9, and so deposited that the
5 particle diameters of the fine particles 9 may produce
convexes.

The electron emission device prepared
according to the above steps 1) to 4) can serve as a
device having far superior characteristics as compared
10 with the conventional device prepared using the
forming. In the electron-emitting device of the
present invention, even the device obtained according
to the steps 1) to 4) can exhibit sufficiently good
characteristics, but more preferred is a device
15 applied with the following step 5), since the extent
of exposure of the fine particles fixed in the
insulating layer can be made adjustable by adjusting
the deposit thickness of the insulating layer and the
amount of etching, and furthermore it becomes possible
20 to control the electric current between electrodes and
also control the amount of electron emission.

5) Etching is applied on the surfaces of the
convexes of the insulating layer 11 obtained in 4).
For example, ion milling may be carried out in the
25 state that the specimen is obliquely set, so that the
surfaces of the convexes of the insulating layer 11

1 are etched. As a result, there is given the structure that part of each fine particle 9 is exposed from the insulating layer 11 at the etched portions and also fixed in the insulating layer 11.

5 In addition, in the above steps 1) to 5), the low-melting glass may be used as the material for the insulating layer 11 and, after step 5) in Fig. 14, the specimen may be baked at a temperature higher than the softening point of the low-melting glass, so that the
10 fine particles 9 can be further firmly fixed in the insulating layer 11 comprised of the low-melting glass. This makes it possible to provide a further stable electron-emitting device.

The electron-emitting device of the present
15 invention may also comprise those as illustrated in Fig. 15 (a) and (b) and Fig. 16 (a) and (b).

In Fig. 15, the numeral 12 denotes a substrate comprising metals 13 such as Ag, Ba, Pb, W and Sn or metal oxides 13 such as BaO, PbO and SnO₂ deposited in
20 porous glass. The numerals 1 and 2 denote electrodes provided on the substrate.

Usable as the above porous glass are ~~Vycor~~ ^{Vycor} glass available from Corning Glass Works or porous glass MPG available from Asahi Glass Co., Ltd., and
25 those having a pore size of from 40 angstroms to 5 μ m, more preferably having a pore size of from 100

1 angstroms to 0.5 μm . Fine particles of metals or
metal oxides of the size equal to or smaller than the
pore size are deposited in the pores. The present
embodiment may not be limited to the porous glass, and
5 may be worked using those obtained by roughening the
glass surface with an aqueous hydrofluoric acid
solution or other porous insulating substrates.

Bringing metals to be deposited and fixed in
the pores of porous glass can be achieved by commonly
10 available methods as exemplified by a method in which
porous glass is impregnated with an aqueous solution
of a nitrate such as AgNO_3 , $\text{Ba}(\text{NO}_3)_2$ and PbNO_3 or an
aqueous sulfuric acid solution, followed by drying and
thereafter baking in a reducing atmosphere. To
15 deposit the metal oxides, the deposited metals may be
baked at a suitable temperature and in an atmosphere
of oxygen.

In bringing the metals or metal oxides to be
projected from the surface of porous glass, the glass
20 surface may be treated for 1 minute with a
hydrofluoric acid solution, followed by washing and
drying. A desired substrate 12 can be thus prepared.

The above substrate 12 may more preferably
have a thickness of 0.5 μm or more because of the
25 roughness on the surface of porous glass.

In Fig. 16, the numeral 14 denotes a glass

1 substrate commonly called as colored glass, which is
glass that contains metal colloid fine particles 15.
The numeral 1 or 2 denotes an electrode provided on
the substrate. The metal colloid fine particles in
5 the colored glass may suitably have a particle
diameter of from 20 angstroms to 6,000 angstroms, more
desirably from 100 angstroms to 2,000 angstroms.
Also, the density of the fine particles, though
variable depending on the particle diameter or
10 materials for the fine particles, may suitably be in
such a state that particles are spatially apart and
electrically connected in the vicinity of a drive
voltage. To make such colored glass, it can be
readily prepared by a commonly often used technique,
15 namely, a method in which colorant raw materials such
as AuCl_3 and AgNO_3 are dissolved in main components of
the glass, which is then subjected to heat treatment
for 10 to 20 minutes at temperatures of from 600°C to
 900°C to deposit gold colloid or silver colloid fine
20 particles in the glass. In the substrate prepared
according to such a commonly available method, the
metal fine particles are little deposited out of the
glass surface, and therefore have good smoothness of
the substrate surface on which the electrodes are
25 formed, thus bringing about the advantage that the
electrodes in this device can be made to have a

1 smaller thickness.

In this device, after the metal fine particles were deposited in the glass, the substrate surface may also be treated with an aqueous hydrofluoric acid
5 solution in the same manner as in the device described in relation to the above Fig. 15 so that the metal colloids may be protruded in a large number from the glass substrate surface, thus obtaining the effect as aimed in the present invention.

10 The present invention further provides an electron-emitting device characterized by a device structure, comprising a semiconductor layer formed between opposing electrodes, and fine particles further arranged in a dispersed state on said
15 semiconductor layer.

In the electron-emitting device of the present invention, application of a voltage between the electrodes brings about emission of electrons from the fine particles which are conductive.

20 Taking such a device structure not only can solve the problems involved in the prior art previously discussed, but also can provide an electron-emitting device capable of obtaining emitted electric currents with a low electric power and in a high
25 density.

Description will be made below on the basis of

1 Fig. 17.

In the figure, electrodes 1 and 2 are provided on a substrate 4, giving minute spacing to form a discontinuous electron-emitting region comprising fine particles 9 dispersed between them. The numeral 16 denotes a semiconductor layer formed at least at an electrode spacing region L.

Fig. 18 is a diagrammatical cross section in the C-D direction in Fig. 17. In the figure, the kind, particle diameter and spacing between fine particles on the substrate 4 are as described in relation to Fig. 8.

A method for preparing of the device illustrated in Fig. 17 will be described below.

15 Fig. 19 (1) to (3) illustrate cross sections of a device for each preparation step.

(1) The surface of a substrate 4 comprised of glass or ceramics is degreased and cleaned.

(2) On the insulating layer obtained in (1), electrodes 1 and 2 are formed according to vacuum deposition, photolithoetching, lifting-off, printing, or the like process.

(3) Next, the fine particles 9 are coated on the electrode gap region obtained in (2). A dispersion of fine particles are used in the coating. Fine particles and an organic binder to promote dispersion

1 of the fine particles are added in an organic solvent
comprised of butyl acetate, alcohol, ketone or the
like, followed by stirring or the like to prepare the
dispersion of fine particles. Usable as the organic
5 binder are butyral resins, acrylic resins, vinyl
chloride-vinyl acetate copolymers, phenol resins,
nylons, polyesters and urethanes.

Here, an example of methods for preparing the
dispersion of the fine particles is set out below.

T380X 10

Fine particles, SnO_2 1 g

(fine particle diameter: 100 to 1,000 angstroms)

Organic solvent, MEK (methyl ethyl ketone) :

cyclohexane = 3 : 1 1,000 cc

T381X

Organic binder, butyral 1 g

15 The above materials were stirred in a paint shaker for
three hours glass beads to make a dispersion.

This fine particle dispersion is coated on the
surface of a specimen according to dipping, spin
coating or the like process, and then baking is
20 carried out for about 10 minutes at a temperature at
which the solvent or the like may be evaporated and
also the organic binder is carbonized to give a
semiconductor layer, for example, at 250°C . Thus the
semiconductor layer 16 and the fine particles 9 are
25 arranged in the electrode spacing L. Of course, the
semiconductor layer 16 and the fine particles 9 are

1 arranged on the whole surface of the specimen, but no
difficulty is brought about as there is applied
substantially no voltage to the semiconductor layer 16
and the fine particles 9 outside the electrode spacing
5 L when electrons are emitted. Thickness of the
semiconductor layer 16 and arrangement density of the
fine particles 9 may vary depending on the coating
conditions and how to prepare the fine particle
dispersion, and the amount of electric currents
10 flowing to the electrode spacing L may also vary in
accordance with this.

In addition to the above formation by coating,
also available as a method for dispersing the fine
particles 9 to the electrode gap region obtained in
15 (2) is, for example, a method in which a solution of
an organic compound is coated on the substrate
followed by thermal decomposition to form metal
particles. As an example, a solution is prepared
using materials shown below:

| | | |
|----|--|---------|
| 20 | Fine particle material: Pd organic metal compound (weight calculated as Pd metal) | 3 g |
| | Organic solvent: Butyl acetate | 1,000 g |
| | Organic binder: Butyral | 1 g |

25 This Pd organic metal compound solution is coated,
followed by heating, so that the fine particles 9

1 comprising Pd and the insulating layer 16 can be
obtained.

The semiconductor layer 16 comprises a film
mainly constituted of the carbon obtained by the
5 baking. This is a semiconductor layer having an
electrical specific resistance of about 1×10^{-3}
ohm.cm or more.

In the specimen obtained according to the
above steps, the thickness of the semiconductor layer
10 16 becomes smaller than the particle diameter of the
fine particles 9. In other words, it has the
structure that the fine particles 9, though embedded
in the semiconductor layer 16, are fixed in the manner
that they are partly protruded. (Fig. 18)

15 In the embodiment having been described above,
the fine particles 9 has the structure that they
protrude from the semiconductor layer 16. Here, the
fine particles 9 may be covered with a carbon film
obtained by further coating only the organic binder
20 solution on the surface of this device followed by
baking, so that there can be given the structure that
the fine particles 9 are included into the
semiconductor layer 16 as illustrated in Fig. 20.

The ratio of carbon to fine particles in the
25 coating solution may be changed to increase the
carbon, and also the amount of coating may be

1 increased, so that there can be also given the
structure that the fine particles 9 are included into
the semiconductor layer 16 or at least part thereof
has protruded from the semiconductor layer as
5 illustrated in Fig. 21.

The devices having been described above has
the feature that the production steps can be
simplified since the semiconductor layer 16 is formed
in the same step as for arrangement of the fine
10 particles 9.

It is also possible to prepare the
semiconductor layer 16 from materials other than the
carbon, namely, semiconductor materials obtained by
coating or printing and baking, as exemplified by a
15 solution containing Si, Ge, Se or the like.

Accordingly, a semiconductor layer having desired
characteristics can be obtained by selecting the
conditions for the preparation and coating of the
solution of these materials and for the baking. Also
20 in using these semiconductor layers, there is retained
the feature that the fine particles can be arranged in
the same step.

The electron-emitting device of the present
invention may also comprise an electron-emitting
25 device having the structure as shown in Fig. 22.

A method of preparing the electron-emitting

1 device illustrated in Fig. 23, 1) to 4) will be described. Cross sections of a device are illustrated in succession to describe below an example of the preparation method.

5 1) The surface of a substrate 4 is degreased and cleaned.

2) On the substrate obtained in 1), formed is a semiconductor layer 16 obtained by vacuum deposition, coating or printing and baking.

10 Usable as the above semiconductor layer are an amorphous silicon semiconductor film or crystallized silicon semiconductor film obtained by vacuum deposition, a compound semiconductor film, and a semiconductor film obtained by coating or printing and
15 baking.

For example, there can be formed a hydrogenated amorphous silicon (A-Si:H) semiconductor layer obtained by plasma CVD. This semiconductor layer has a film thickness of approximately from 50
20 angstroms to 10 μm .

3) Electrodes 1 and 2 are provided in the same manner as in (2) in Fig. 19.

4) Fine particles 9 are provided in the same manner as in (3) in Fig. 19. It is preferred to
25 decrease the amount of carbon in the coating solution or reduce it to zero to make small the thickness of

1 the carbon film semiconductor layer formed at the
electrode spacing region L. This is because the
effect of the semiconductor layer 16 can be better
brought out by allowing an electric current I_f flowing
5 to the electrode spacing L to flow to the
semiconductor layer 16 and the fine particles 9 as
much as possible.

In the device having such structure, it is
also possible to use fine particles feasible for
10 vacuum deposition. With a material applicable to
vacuum deposition, the fine particles can be formed by
control of vacuum deposition conditions such as
substrate temperature or by a means like vacuum
deposition such as masked vacuum deposition.

15 In the electron-emitting device obtained
according to the above 1) to 4), the semiconductor
layer and the fine particles are each formed in a
separate step, resulting in a greater degree of
freedom in the conditions for forming the
20 semiconductor layer. Accordingly, it becomes more
possible to adjust characteristics of the
semiconductor layer 16. For example, changing the
amount of an impurity dope and selecting suitable
conditions for formation in forming a semiconductor
25 makes it able to readily adjust the electrical
resistance of the semiconductor layer 16.

1 Accordingly, it becomes feasible to adjust the amount
of the electric current I_f flowing to the device, thus
bringing about the feature that it becomes feasible to
adjust the drive voltage of the device.

5 In the electron-emitting device of the present
invention, the substrate itself may also comprise a
semiconductor substrate that replaces the
semiconductor layer 16. Fig. 24 illustrates a cross
section of the device of this embodiment. As the
10 semiconductor substrate 17, there can be used
substrate materials having desired characteristics, as
exemplified by Si wafers. Usable as methods for
obtaining the semiconductor substrate having the
desired characteristics are ion implantation to a
15 semiconductor substrate or insulator substrate and the
like methods.

This method enables adjustment of the specific
resistance only at desired areas on the same plane.
For this reason, in instances where electron-emitting
20 devices are integrated in a high density, the leakage
current among adjacent devices can be made small and
the crosstalk can be decreased. Because of the
arrangement on the same plane, this method further has
the feature that no trouble such as disconnection may
25 occur owing to poorness in step coverage on the
stepped ends of the electrodes.

1 Fig. 25 is a cross section explanatory of
still another electron-emitting device of the present
invention. The respective materials are constituted
in the manner as described above, but in the
5 preparation steps the semiconductor layer 16 is formed
after the electrodes 1 and 2 and the fine particles 9
were formed. Thus the fine particles 9 are made to be
included into the semiconductor layer 16 and fixed
there. The surface of the semiconductor layer is
10 thereafter shaved off by etching to give the structure
that the fine particles 9 are fixed in the state that
they protrude from the semiconductor layer.

Fig. 26 (1) to (5) successively illustrate
cross sections of device to explain the preparation
15 steps of the electron-emitting device illustrated in
Fig. 5. An example of the preparation method will be
described below.

- (1) The surface of the substrate 4 is degreased
and washed.
- 20 (2) Electrodes 1 and 2 are provided in the same
manner as in Fig. 19(2).
- (3) Fine particles 9 are provided in the same
manner as in Fig. 19(3) (preferably using a dispersion
containing no organic binder).
- 25 (4) A semiconductor 16 is formed in the vicinity
of the electrode spacing region L. Here, in general,

1 the semiconductor layer is deposited also on the
surface of the fine particles 9, and so deposited that
the particle diameters of the fine particles 9 may
produce convexes.

5 (5) Etching is applied mainly on the surfaces of
the convexes of the semiconductor layer 16 obtained in
(4). For example, ion milling may be carried out in
the state that the specimen is obliquely set, so that
the surfaces of the convexes of the semiconductor
10 layer 16 are etched. As a result, there is given the
structure that part of each fine particle 9 is exposed
from the semiconductor layer 16 at the etched portions
and also fixed in the semiconductor layer 16.

If alternatively the etching step is not
15 applied, there is given the structure that the fine
particles 9 are included into the semiconductor layer
16.

In all the embodiments having been described
above, the semiconductors and fine particles are
20 arranged in the electrode spacing region formed on a
plane substrate, but the present invention is by no
means limited to these forms.

For example, the electron-emitting device may
take the form as shown in Fig. 1, i.e., the vertical
25 type one. (See Fig. 27.) This is a device in which
the electrodes 1 and 2 are each formed on the other

1 side of a stepped portion of the insulating layer 5 on
the substrate 4.

The present invention particularly further
provides a device in which the electrodes disposed in
5 the electron-emitting device as illustrated in Fig. 8
are made to be disposed as in the vertical type as
shown in Fig. 1, i.e., an electron-emitting device
comprising a substrate provided thereon with an
insulating layer in which fine particles are
10 dispersed, a stepped portion formed at an end portion
of the insulating layer on the top surface of the
substrate, and an electrode provided each on the top
surface of said insulating layer and on the top
surface of said substrate; an end of each electrode
15 being positioned at an upper end or lower end of said
stepped portion in such a manner that at least part of
the sidewall face at the stepped portion, of the end
portion of said insulating layer in which the fine
particles are dispersed may not be hidden; and
20 electrode spacing being formed between said electrode
ends, where electrons are emitted by applying a
voltage between these electrodes [Fig. 28 (C)].

In Fig. 28 (a), (b) and (c), the numerals 1
and 2 denote electrodes for obtaining electrical
25 connection; 4, a substrate; 9, fine particles; 5, an
insulating layer containing the fine particles in a

1 dispersed state; and 6, an electrode spacing.

In Fig. 28 (C), the electron-emitting device of the present invention is a device such that the fine particles 9 dispersed in the insulating layer 5 forming a stepped portion are arranged at the electrode spacing 6 formed between the electrodes 1 and 2 whose end portions oppose each other (but without overlap) at the stepped portion, where electrons are emitted from the fine particles 9 by applying a voltage between the electrodes 1 and 2.

An example of preparation methods will be described below in relation to Fig. 28 (a), (b) and (c).

First, the insulating layer 5 containing the fine particles 9 is built up on the substrate 4 by liquid coating or a like process [see Fig. 28 (a)].

Next, the insulating layer 5 is etched by photolithoetching so that a stepped portion is given substantially at the middle portion of the substrate 4 [see Fig. 28 (b)].

Then the electrodes 1 and 2 are deposited on the insulating layer 5 and the substrate 4 in such a manner that at least part of the sidewall of the stepped portion may not be hidden, thus forming the electrode spacing 6 [see Fig. 28 (c)].

The electron-emitting device of the present

1 invention can be obtained according to the above
process. The present device may be placed in a vacuum
container, a voltage may be applied to the electrodes
1 and 2, and a lead-out electrode plate (not shown)
5 may be disposed so as to oppose at the top surface of
the device, to which a high voltage is applied,
whereupon electrons are emitted from the vicinity of
the electrode spacing 6.

In this figure, the materials for and
10 thickness of the electrodes, materials for the fine
particles concerned with the electron emission and
materials for and thickness of the insulating layer
are as described in relation to Fig. 1.

It can be confirm that an electron-emitting
15 device comprising electrodes 1 and 2 formed partly
overlapping as illustrated in Fig. 29 (c), though
having a slight difference in the electrode spacing,
can also give good results.

In the device illustrated in Fig. 29 (c), an
20 electrode 1 is first deposited and formed on a
substrate 4 [see Fig. 29 (a)]. Thereafter an
insulating layer 5 containing fine particles 9 and an
electrode material 2c are deposited [see Fig. 29 (b)],
and an electrode 2 and electrode spacing 6 are formed
25 by photolithoetching, thus forming an electron-
emitting device [see Fig. 29 (c)].

1 The present invention also provides an
electron emission device as illustrated in Fig. 30,
which is another embodiment of the electron-emitting
device described in relation to Fig. 28 and at the
5 same time a preferred embodiment of the electron-
emitting device illustrated in Fig. 1.

 The electron-emitting device illustrated in
Fig. 30 comprises a substrate provided thereon with
insulating layers interposing the face on which fine
10 particles are dispersed, a stepped portion formed
between an end portion of the insulating layer and the
top surface of the substrate, and an electrode
provided each on the top surface of said insulating
layer and on the top surface of said substrate; an end
15 of each electrode being positioned at an upper end or
lower end of said stepped portion in such a manner
that said electrode may not come into contact with the
face on which the fine particles are dispersed; and
electrode spacing being formed between said electrode
20 ends, where electrons are emitted by applying a
voltage between these electrodes.

 In Fig. 30, the numeral 1 and 2 denote
electrodes for obtaining electrical connection; 4, a
substrate; 5a, an insulating layer on the substrate 4;
25 9, fine particles on the insulating layer 5a; 5b, an
insulating layer to cover the fine particles; and 6,

1 electrode spacing between the electrodes 1 and 2.

In Fig. 30(d), the electron-emitting device of the present invention is a device in which the fine particles 9 interposed between the insulating layers 5a and 5b are arranged at the electrode spacing defined between the electrodes 1 and 2 whose end portions oppose each other (but without overlap) at the stepped portion, and electrons are emitted from the fine particles 9 by applying a voltage between the 10 electrodes 1 and 2.

A preparation method thereof will be described below.

First, the insulating layer 5a is built up or deposited on the substrate by liquid coating, vacuum 15 deposition or the like process, and then the fine particles 9 are dispersed on the insulating layer 5a [see Fig. 30 (a)].

Next, the insulating layer 5b is built up or deposited on the insulating layer 5a and the fine 20 particles 9 by liquid coating or vacuum deposition or the like process so that it may cover the fine particles 9 [see Fig. 30 (b)].

The insulating layers 5a and 5b interposing the fine particles are further formed by 25 photolithoetching so that the stepped portion can be given substantially at the middle of the substrate 4

1 [see Fig. 30 (c)].

Thereafter, the electrodes 1 and 2 are deposited on the insulating layer 5b and the substrate 4 in such a manner that at least part of the sidewall 5 of the stepped portion and the fine particles 9 may not be hidden and also no electric short may be caused, to form the electrode spacing 6 [see Fig. 30 (c)]

The electron-emitting device of the present 10 invention can be obtained according to the above process. The present device may be placed in a vacuum container, a voltage may be applied to the electrodes 1 and 2, and a lead-out electrode plate (not shown) may be disposed so as to face the top surface of the 15 device, to which a high voltage is applied, whereupon electrons are emitted from the vicinity of the electrode spacing 6.

The present invention may still also be embodied for the electron-emitting region 3 by forming 20 an electron-emitting layer 3a and electron-emitting bodies 3b.

For example, as illustrated also in Fig. 31, this is an electron-emitting device having the structure that, for example, the embodiments of Fig. 3 25 and Fig. 5 previously described are combined.

In Fig. 31, the electron-emitting device of

1 the present invention is a device comprising a
laminate comprising an insulating layer 5 held between
a pair of electrodes whose end portions oppose each
other, wherein the electron-emitting layer 3a is
5 included into the insulating layer 5 in such a manner
that the sidewall face of the electron-emitting layer
3 a may be disposed along the sidewall face of the
insulating layer 5 formed at the opposing portion at
which the electrodes 1 and 2 oppose each other, and
10 the electron-emitting bodies 3b are further disposed
at the surface of said sidewall, where electrons are
emitted by applying a voltage between the electrodes 1
and 2.

The materials and methods for forming the
15 device are as described previously.

Besides taking the structure as illustrated in
Fig. 31 to form the electron-emitting region 3, it is
also desirable to, as shown in Fig. 33, form a stepped
portion 18 with an insulating layer 5 containing fine
20 particles (electron-emitting materials) 9 and at the
same time provide electron-emitting bodies 3b on the
side surface of said stepped portion.

Alternatively, as shown in Fig. 35, fine
particles (electron-emitting materials) 9 may be
25 arranged on an insulating layer 5a, the fine particles
are further covered thereon with an insulating layer

1 5b to form a stepped portion, and electron-emitting
bodies 3b may be further arranged on the side surface
of said stepped portion to form an electron-emitting
region.

5 In the present invention, the device may also
comprise an electron-emitting region obtained by three
or more of its formation methods as shown in Fig. 36.

Incidentally, in the case where the fine
particles are used as the electron-emitting bodies 3b
10 dispersed on the side surface or the electron-emitting
materials 9 contained in the insulating layer as
described above, it was confirmed that employment of
two or more kinds of different materials as said fine
particles enables better control of the
15 characteristics as the electron-emitting device.

Usable as materials for the fine particles are
the materials same as those described in relation to
Fig. 8. Selecting appropriately two or more kinds of
different materials among those materials as occasion
20 demands and using them as the fine particles makes it
possible to not only achieve electron emission but
also improve or control the characteristics of
intended electron-emitting devices.

For example, since in the electron-emitting
25 device of the present invention an electric current in
the direction of electrodes is indispensable for

1 electron emission, it is possible to lower the drive
voltage of the device by incorporating fine particles
of relatively low resistance nature (for example,
incorporating Pd or Pt fine particles in SnO_2 fine
5 particles).

It can be also expected to increase electron
emission by adding to Pd fine particles, low work
function materials as exemplified by LaB_6 or materials
having a large coefficient of secondary electron
10 emission as exemplified by an AgMg alloy.

The present invention can be also effective
not only for the embodiment using the fine particles
of two or more of different materials, but also for
the instance where the fine particles, even though
15 comprised of one kind of materials, are constituted of
two or more kinds having difference only in physical
parameters such as average particle diameter and
shapes.

For example, the particle diameter may be made
20 to comprise two kinds, one of which is so fine (as
exemplified by a particle diameter of about 100
angstroms) that the effect of electric field emission
can be greatly exhibited, and the other of which is
relatively so large (as exemplified by a particle
25 diameter of about 4,000 angstroms) as to be
contributory only to electrical conductivity, so that

1 the former can realize increase in the amount of
electron emission, and the latter, driving with a low
voltage.

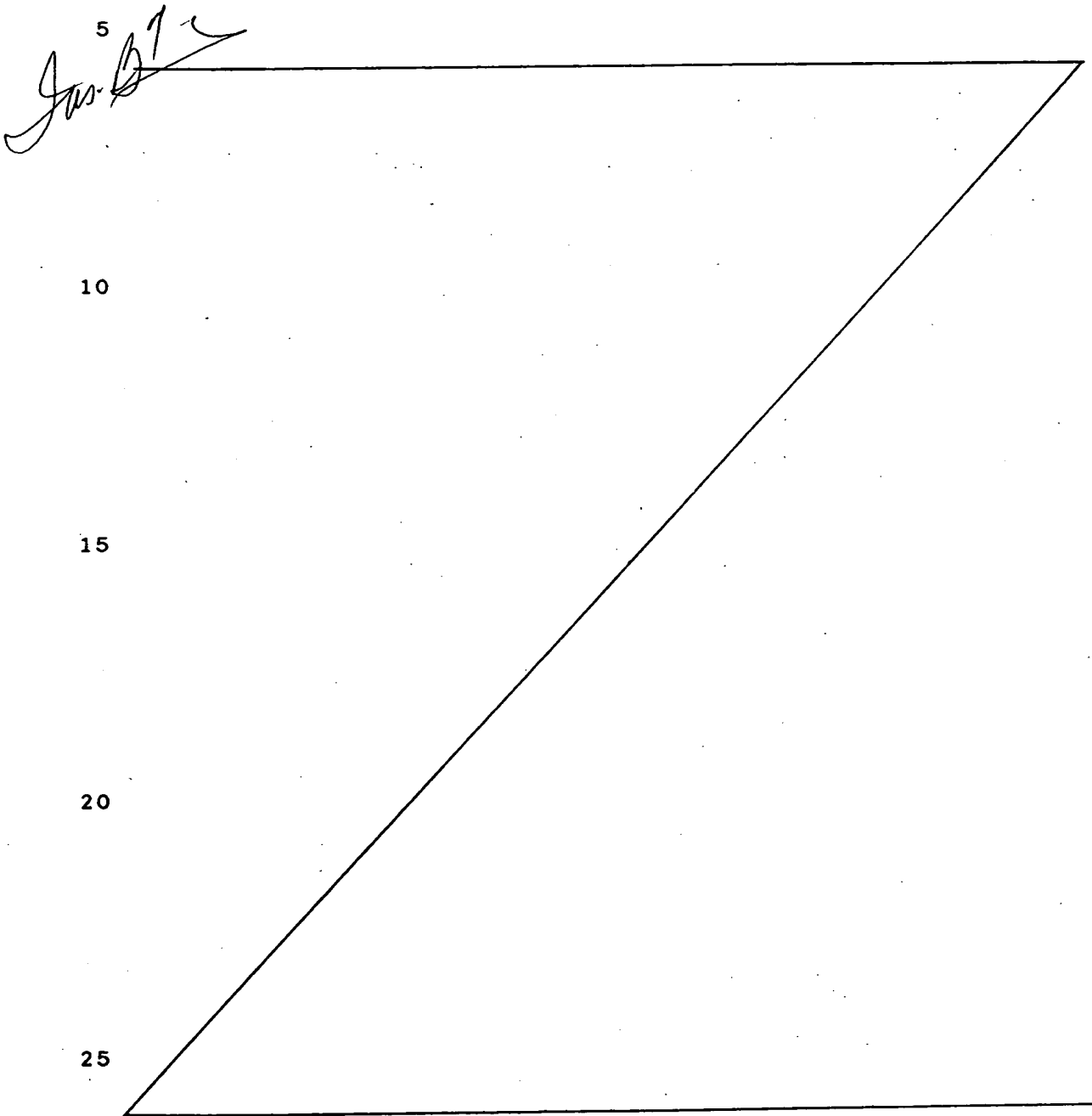
It is of course also possible to utilize the
5 materials by making combination both of the above-
described two or more kinds of different materials and
two or more kinds having difference in physical
parameters as in particle diameter.

To form the fine particles by dispersion, most
10 simple and convenient is a method in which a
dispersion of fine particles comprising desired
materials is coated on a substrate or the like by
rotary coating, dipping or the like technique,
followed by heating to remove a solvent, a binder and
15 so forth. In this instance, adjusting the particle
diameter of fine particles, content thereof, coating
conditions, etc, enables control of the state of
distribution of their dispersion.

There is no established theory as to the
20 mechanism by which the electrons are emitted from the
electron-emitting device according to the present
invention, but it is presumed to be nearly as follows:

Presumed are the electric field emission
because of the voltage applied to a narrow insulating
25 layer gap, or the secondary electron emission
occurring when the electrons emitted from electron-

1 emitting materials are diffracted or scattered by the
film of the island-like structure or the electrodes,
or caused by collision, or the thermionic emission,
hopping electrons, Auger effect, etc.



1 EXAMPLES

Specific examples of the present invention will be described below.

Example 1

5 Fig. 3 (a), (b) is a flow sheet illustrating an example for a method of preparing the electron-emitting device of the present invention.

In Fig. 3 (a), (b), the numeral 4 denotes a glass substrate; and 1, a nickel electrode of 500
10 angstroms thick.

SiO_2 was vapor deposited to form an insulating layer 5a of 1,000 angstroms thick, Au was vapor deposited as an electron-emitting layer 3a to have a thickness of 500 angstroms, and an insulating layer 5b
15 was also formed in the same manner as for 5a, thus bringing these three layers into lamination.

Then these were partly laminated on the electrode 1 as illustrated in Fig. 3 (a), along the pattern of the electrode 1, followed by patterning.
20 Next, Ni was laminated as an electrode 2 with a film thickness of 5,000 angstroms.

As illustrated in Fig. 3 (b), the electrode 2 was subjected to patterning by usual photolithographic process along the patterns of the electrode 1,
25 insulating layer 5a, electron-emitting layer 3a and insulating layer 5b. As illustrated in the figure,

58

1 the electrodes 2a and 2b were electrically separated,
and here the area at which the electrode 2b and
electrode 1 overlap was made as small as possible.

Applying a voltage of 20 V between the
5 electrode 2a and 2b, there was obtained emission of an
electron beam 7 of 0.3 μ A per 1 mm length of width of
the electrode 2a in the direction vertical to the
paper surface.

As to the electron-emitting layer 3a, usually
10 it may show an island structure similar to the small
island structure among narrow cracks in the
conventional film prepared by forming, if its film
thickness is 100 angstroms or less. However, it is
presumed that even if the film thickness increases to
15 give a continuous film, the electrodes 1 and 2b are
electrically insulated, and thus the layer acts
similarly to the island structure.

Example 2

In Fig. 4, the numerals 1 to 5 denotes the
20 same as in Fig. 3. In this figure, the numeral 8
denotes an intermediate layer, which is interposed
between the insulating layer 5b and electrode 2 to
constitute a multi-layer electrode. In the present
Example, subsequent to the formation of the insulating
25 layer 5b, a step to vapor-deposit LaB_6 to a thickness
of 1,000 angstroms followed by patterning was added to

1 the preparation steps in Example 1. The electrode 2
was also formed by using Ni with a thickness of 5,000
angstroms as in Example 1.

Applying a voltage of 20 V between the
5 electrode 2a and 2b of the device thus obtained, there
was obtained emission of an electron beam 7 of 0.5 μ A
per 1 mm length of width of the electrode 2a in the
direction vertical to the paper surface.

Example 3

10 Fig. 6 (a), (b) is a flow sheet illustrating
an example for a method of preparing the electron-
emitting device according to the second embodiment of
the present invention. In Fig. 6 (a), (b), the
numeral 4 denotes a glass substrate.

15 An insulating layer 5a was formed with SiO_2 in
1,500 angstrom thickness; an electron-emitting layer
3a, with Pd in 250 angstrom thickness; and an
insulating layer 5b, with SiO_2 in 500 angstrom
thickness, each of which layer was obtained by vacuum
20 deposition and thereafter, as illustrated in Fig. 6
(a), etched to have a stepped shape to effect
patterning. Next, electrodes 1 and 2 are deposited.
The electrodes are, as illustrated in fig. 6 (b), are
deposited on the insulating layer 5a and 5b and the
25 stepped portion formed by the electron-emitting layer
3a with use of Ni with a thickness of 1,000 angstroms.

1 In this occasion, generally the electrode 1 will not
come into contact with the electron-emitting layer 3
if the thickness of the electrode is made smaller than
the height of the stepped portion of the insulating
5 layer 5a, i.e., the step coverage is made poor, and
also the electrode spacing 6 can be made narrower if
the insulating layer 5b is made thinner.

The electron-emitting device obtained
according to the above process was placed in vacuum, a
10 voltage of 1 kV was applied using a lead-out electrode
(not shown) provided at an upper area in the drawing,
and a direct current voltage of about 12 V was applied
between the electrodes 1 and 2, resulting in emission
of electrons from the electron-emitting region 3.

15 Example 4

(See Fig. 2.) On a glass substrate 4, an
insulating layer 5 was deposited using SiO_2 to a
thickness of 2,000 angstroms. This was etched to have
a stepped shape to effect patterning. Next,
20 electrodes 1 and 2 were deposited with Ni in 1,000
angstroms thickness by vacuum deposition with masking
to desired shapes. Here, the step coverage by vapor
deposited Ni at the stepped portion was generally made
poor, and the electrode spacing 6 was formed in a
25 space of about 1,000 angstroms. Fine particles were
made to be fixed here as electron-emitting bodies 3b.

1 The fine particles are obtained, for example, by the
following manner. Namely, prepared is a solution of
fine particles of metals such as Pd, having a particle
diameter of several 100 angstroms as materials serving
5 as the electron-emitting bodies 3b. This solution was
coated by spin coating, and baked at a temperature of
about 300°C to fix the fine particles to the electrode
spacing region. The resulting device was able to emit
electrons by driving it as in Example 3.

10 Example 5

In the constitution in Fig. 8, formed on a
soda lime glass substrate 4 was an insulating layer 11
comprised of a lead oxide type low-melting glass
coating film.

15 Pt electrodes 1 and 2 were further formed
thereon with a thickness of 1,000 angstroms, $L = 0.5$
 μm and $W = 300 \mu\text{m}$, and Pd, as fine particles 9, of
several hundred angstroms in particle diameter were
further arranged in a dispersed state between said
20 electrodes.

The Pd fine particles 9 were arranged by spin
coating (3,000 rpm; coating was repeated five times),
using a butyl acetate solution (Catapaste CCP-4230,
available from Okuno Seiyaku Kogyo) containing an

1 organic palladium compound in an amount of about 0.3 %
in terms of Pd metal, and treated by heating at 250°C.
They were then baked for 20 minutes at 450°C to bring
the fine particles to be included into the insulating
5 layer 11.

Here, the amount of an electric current
flowing to the electrode spacing L was about 5 $\mu\text{A}/5\text{V}$.
This specimen was subjected to pickling using an
aqueous 5 to 10 vol.% HCl solution, resulting in the
10 amount of electric current of 250 $\mu\text{A}/5\text{V}$.

The specimen prepared according to the above
process was placed under vacuum of 10^{-5} Torr or more,
and a voltage was applied between the electrodes 1 and
2 as described above. As a result, an electric
15 current V_f flowed on the surface of inside of the
insulating layer 11 or through the fine particles 9,
and a stable electron emission was confirmed when a
voltage was applied allowing an lead-out electrode
(not shown) to serve as the anode. The electron
20 emission was also confirmed in regard to a specimen to
which no pickling was applied.

Results of measurement on the electron-
emitting device prepared in the present Example are
shown in Table 1. Swing of the emitted electric
25 current is indicated with a value obtained by dividing

1 the amount of change ΔI_e in the amount of the emitted electric current of 1×10^{-3} Hz or less by the emitted electric current I_e and multiplying it by 100, i.e., $\Delta I_e / I_e \times 100$.

5

Table 1

| 10 | V_f | I_e | Efficiency | | Swing |
|---------|----------|---------|--------------------|---------|---------|
| | Device | Emitted | (Emitted | Life* | |
| | drive | current | current I_e | | of |
| | voltage | current | current I_f) | | emitted |
| | | | | | current |
| Present | | | | | |
| 15 | Example: | μA | | | |
| | 30 V | 0.8 | 8×10^{-3} | 100 hrs | 10 % |
| | | | | or more | |

* Life: The period in which the emitted electric current comes to 50 % or less

20 The above results, as compared with the results of measurement of a surface conduction electron-emitting device comprised of ITO materials that required the forming the conventional technique (drive voltage of the device: 20 V; emitted electric

25 current: $1.2 \mu A$; efficiency: 5×10^{-3} , life: 35 hours; swing of emitted electric current: 20 to 60 %), can

1 tell the following:

The electron-emitting device of the present Example is stable and of long life, and shows high characteristics in the electron-emitting efficiency.

5 Example 6

Example 5 was exactly repeated except that the baking for 20 minutes at 450°C was replaced by complete baking for 2 hours at 490°C, to carry out an experiment.

10 The device obtained by the above experiment gives a device in which all the fine particles 9 are penetrated into the insulating layer 11 (Fig. 9).

The same measurement as in Example 5 was made on this electron-emitting device to obtain the same
15 electron emission as in Example 5, but it tended to have a longer life and show further decreased swing of the emitted electric current.

More specifically, the electron-emitting device in which the fine particles are included into
20 the insulating layer as in the present Example 6 is characterized by being more improved in the life and the swing of emitted electric current in addition to the effect obtainable in Example 5.

1 Example 7

Example 5 was exactly repeated except that the baking for 20 minutes at 450°C was replaced by baking for 10 minutes at 420°C.

5 The device obtained by the above experiment gives a device as shown in Fig. 10. The electron-emitting device in which the fine particles are slightly penetrated into the insulating layer brought about an electron-emitting device having more improved
10 emitted electric current and emitted current efficiency (I_e/I_f) in addition to the effect obtainable in Example 4.

Example 8

 The surface of the insulating layer 11 at the
15 electrode spacing L of the electron-emitting device obtained in Example 6 was etched using an aqueous 5 Vol.% Hf solution to bring the fine particles 9 to expose from the insulating layer 11, so that there was obtained a device having the same structure as in the
20 above Example 7.

Example 9

 Using a substrate 12 comprising porous glass having a pore size of 80 to 1,000 angstroms in which gold fine particles were deposited to have a device
25 resistance of from 1 megaohm to 10 megaohms, there was given an electron-emitting device of the present

1 invention (Fig. 9).

Measurement on said device was carried out in the same manner as in Example 5. Results are shown in Table 2.

Table 2

| | V_f | I_e | Efficiency (Emitted current $I_e /$ Device current I_f) | Life* |
|---------|----------------------------|--------------------|--|-----------|
| 10 | Device drive voltage | Emitted current | Device current I_f) | |
| <hr/> | | | | |
| Present | | | | |
| 15 | Example: | μA | | |
| | 25 V | 1.0 | 2×10^{-3} | 1,000 hrs |
| <hr/> | | | | |
| or more | | | | |

* Life: The period in which the emitted electric current comes to 50 % or less.

20

It was revealed from the above results that the electron-emitting device of the present invention becomes an electron-emitting device that is stable (i.e. small in the swing of the emitted electric current) and of long life and has a high electron emission efficiency as compared with a conventional

1 device obtained by forming of gold (device drive
voltage of: 16 V; emitted current: 0.8 μ A; efficiency:
1.2 x 10⁻⁵; life: 35 hours; swing: 20 to 60 %). After
the experiment for electron emission, the degree of
5 device deterioration was observed by using a scanning
type electron microscope, but there was seen little
change in the diameter or distribution of the fine
particles of gold present between the electrodes.
However, the device obtained by forming of gold showed
10 an extreme deterioration at the high resistance part
discussed in the prior art.

The device according to the present Example 9
was able to be readily intergrated with less
irregularities between devices even when a number of
15 the devices were formed on the same substrate.

Example 10

Referring to Fig. 16, obtained was an electron-
emitting device comprising a colored glass (golden red
glass) substrate 14 having gold colloids.

20 The same measurement as in Example 5 was made
on said electron-emitting device. Results obtained
are shown in Table 3.

1

Table 3

| 5 | V_f | I_e | Efficiency | |
|---------|---------------|---------|--|-----------|
| | Device | Emitted | (Emitted current I_e / current I_f) | Life* |
| | drive voltage | current | Device current I_f | |
| <hr/> | | | | |
| Present | | | | |
| 10 | Example: | μA | | |
| | 32 V | 0.6 | 2×10^{-2} | 2,000 hrs |
| | | | | or more |

* Life: The period in which the emitted electric current comes to 50 % or less.

15

As will be seen also from Table 3, the electron-emitting device of the present Example is stable (i.e. small in the swing of the emitted electric current) and of long life and has a high electron emission efficiency. After the experiment for electron emission, the degree of device deterioration was also confirmed by using a scanning type electron microscope, but there was seen little change in the diameter or distribution of the fine particles of gold present between the electrodes. In contrast therewith, the conventional device obtained by forming of ITO shows an extreme deterioration at

1 the high resistance part.

There was also obtained similar results in the case when, after fine particles are deposited in the glass, the substrate surface was treated with an aqueous hydrofluoric acid solution so that metal colloids may be protruded in a large number from the surface of the glass substrate, thus giving an electron-emitting device of the present invention.

Example 11

10 On a clean, quartz glass substrate of about 1 mm thick, a solution prepared by mixing an organic solvent (Catapaste CCP, available from Okuno Seiyaku Kogyo) containing an organic palladium compound with a SiO_2 liquid coating preparation (OCD, available from Tokyo Ohka Kogyo) to have a molar ratio of SiO_2 : Pd 15 of about 5 : 1 was spin-coated with a spinner. Thereafter the resulting coating was baked for 1 hour at about 400°C to obtain a SiO_2 insulating layer 11 having a film thickness of about 1,000 angstroms and 20 containing Pd fine particles 9. After this step, the surface of the insulating layer 11 was etched using an aqueous hydrofluoric acid to bring the fine particles 9 to protrude from the insulating layer 11.

Next, on the SiO_2 insulating layer 11, a photoresist was formed by photolithography with a thickness of about $0.8 \mu\text{m}$ in the shape giving an

70

1 electrode spacing L . Further on the SiO_2 insulating
layer 11 and said photoresist, a Ni thin film was
deposited with a thickness of 1,000 angstroms
according to the masking EB vacuum deposition that
5 obtains shapes of electrodes. Thereafter the
photoresist was peeled to carry out a lift-off step to
remove unnecessary Ni thin film on the photoresist.
Thus the shapes of the electrodes 1 and 2 and
electrode spacing L as shown in Fig. 8 can be formed.
10 In this instance, each dimension shown in Fig. 8 was
set to be $L = 0.1 \mu\text{m}$, $W = 300 \mu\text{m}$ and $A = 2 \text{ mm}$.

Electron emission characteristics of the
electron-emitting device obtained according to the
above process were measured to have revealed that
15 there was obtained electron emission of,
approximately, emitted electric current $I_e = 1 \mu\text{A}$ and
emission efficiency $\alpha = 5 \times 10^{-3}$ under the drive
voltage $V_f = 30 \text{ V}$ of the device. The life and the
swing of the emitted electric current were in
20 substantially the same level as those in Example 5.

Example 12

Example 11 was repeated but replacing the
organic palladium compound by SnO_2 fine particles of
100 angstroms in average particle diameter, to obtain
25 a similar electron-emitting device, and similar
experiments were carried out. As a result there was

71

1 obtained electron emission of substantially the same
level as in Example 11.

Example 13

In the constitution as illustrated in Fig. 17,
5 a semiconductor layer 16 of about 100 angstroms thick
was formed on a soda glass substrate 4 by using a
carbon film obtained from a calcined organic
substance. Palladium fine particles of about 100
angstroms in diameter are dispersed in the
10 semiconductor layer.

Electrodes 1 and 2 were also formed with Pt to
have a thickness of 1,000 angstroms, a spacing of 0.8
 μm , and a width of 300 μm .

Applying a voltage between the electrodes 1
15 and 2 prepared in the above produced a flow of an
electric current I_f through the semiconductor layer 16
and fine particles 19, and a stable electron emission
was confirmed when a voltage was applied allowing an
lead-out electrode to serve as the anode.

20 Comparison of examples of characteristics were
made between the electron-emitting device prepared in
the present Example, having a semiconductor, and a
prior art surface conduction electron-emitting device
comprised of ITO and requiring the forming, to obtain
25 the results shown in Table 4. Swing of the emitted
electric current is indicated with a value obtained by

1 dividing the amount of change ΔI_e in the amount of the emitted electric current of 1×10^{-3} Hz or less by the emitted electric current I_e and multiplying it by 100, i.e., $\Delta I_e / I_e \times 100$ (%).

5

Table 4

| 10 | V_f | I_e | Efficiency (Emitted current I_e / Device Life* current I_f) | | Swing of emitted current |
|---------|------------------------------|--------------------|--|---------|-----------------------------------|
| | Device drive voltage | Emitted current | Device current I_f) | Life* | |
| T730X | | | | | |
| Present | | | | | |
| 15 | Example: | | | | |
| | 15 V | 4 μ A | 1×10^{-3} | 800 hrs | 15 % |
| | | | | or more | |
| | Device of forming of ITO: | | | | |
| | | | | | % |
| 20 | 20 V | 1.2 μ A | 5×10^{-3} | 35 hrs | 20 - 60 |

* Life: The period in which the emitted electric current comes to 50 % or less

As will be clear from Table 4, the surface
25 conduction electron-emitting device of the present
Example is characterized by being stable and of long

1 life, showing a low drive voltage and a large emitted
electric current.

Example 14

In the constitution illustrated in Fig. 22, an
5 A-Si:H film was deposited on a glass substrate 4 by
plasma CVD to have a thickness of 2,000 angstroms,
thus giving a semiconductor layer 16. Electrodes 1
and 2 were formed with Pt to have a thickness of 1,000
angstroms, a spacing L of 0.8 μm , and a width W of 300
10 μm .

Pd, as fine particles 9, of several 100
angstroms in diameter were further arranged in a
dispersed state between said electrodes.

The Pd fine particles 9 were arranged by spin
15 coating (3,000 rpm; coating was repeated five times),
using a butyl acetate solution (Catapaste CCP-4230,
available from Okuno Seiyaku Kogyo) containing an
organic palladium compound in an amount of about 0.3 %
in terms of Pd metal, and treated by heating at 250°C.
20 The electron-emitting device prepared in the present
Example, having a semiconductor, was evaluated in the
same manner as in Example 13. As a result, it was
able to obtain similar electron emission.

Example 15

25 In the constitution illustrated in Fig. 25,
electrodes 1 and 2 were formed on a glass substrate 4

1 with Pt to have a thickness of 1,000 angstroms, a
spacing L of 0.8 μm , a width W of 100 μm .

Fine particles were prepared in the same
manner as in Example 14, and hydrogenated amorphous
5 silicon was formed as a semiconductor layer 16 by
plasma CVD to have a thickness of about 500 angstroms.

Thereafter the convexes on the semiconductor
layer 16 were etched by ion milling.

The electron-emitting device prepared
10 according to the above process was evaluated in the
same manner as in Example 12 to have found that there
is obtained similar electron emission. Particularly
in the present Example, different from Example 14, the
electron-emitting device in which the fine particles 9
15 were fixed in the semiconductor layer 16 had a
tendency of stableness in electron emission in
addition to the effect obtainable in Example 14.

Example 16

An electron-emitting device was obtained
20 according to the previously described preparation
steps (a) to (c) of Fig. 28.

More specifically, on a clean, quartz glass
substrate of about 1 mm thick, a solution prepared by
mixing an organic solvent (Catapaste CCP, available
25 from Okuno Seiyaku Kogyo) containing an organic

1 palladium compound with a SiO_2 liquid coating
preparation (OCD, available from Tokyo Ohka Kogyo) to
have a molar ratio of SiO_2 : Pd of about 5 : 1 was
spin coated with a spinner. Thereafter the resulting
5 coating was baked for 1 hour at about 400°C to obtain
a SiO_2 insulating layer 5 having a film thickness of
about 1,500 angstroms and containing Pd fine particles
9 [see Fig. 28 (a)].

Next, the insulating layer 5 was etched by
10 photolithoetching with use of an aqueous hydrofluoric
acid solution to form a stepped portion of about 1,500
angstroms high at the middle of the substrate 4 [see
Fig. 28 (b)].

Thereafter, Ni electrodes 1 and 2 of about 500
15 angstroms in film thickness was formed by deposition
utilizing EB vacuum deposition in the manner that the
stepped portion may not be completely covered.

In this instance, there is given the structure
that the electrodes 1 and 2 oppose each other with
20 certain spacing, across the side wall of the stepped
portion of the insulating layer 5 containing the fine
particles 9. This space is designated as electrode
spacing 6 [see Fig. 28 (c)].

Electron emission characteristics of the
25 electron-emitting device obtained according to the
above process were measured to have revealed that

1 there was obtained electron emission of,
approximately, emitted electric current $I_e = 2.5 \mu A$
and emission efficiency $\alpha = 5 \times 10^{-3}$.

Example 17

5 According to the previously described
preparation steps (a) to (c) of Fig. 29, prepared was
an electron-emitting device of the constitution that
an insulating layer is held between electrodes.

More specifically, on a clean, quartz glass
10 substrate 4 of about 1 mm thick, an Ni electrode of
about 500 angstroms in film thickness was deposited by
EB vacuum deposition to form an electrode 1 by
photolithoetching [see Fig. 29 (a)].

Next, on the surface of the electrode 1 and
15 the substrate 4, a SiO_2 insulating layer 5 containing
Pd fine particles 9 was deposited in the same manner
as in Example 16 to have a film thickness of about
1,000 angstroms. A Ni thin film of about 1,000
angstroms in film thickness was further deposited on
20 the SiO_2 insulating layer to give an electrode
material 2c [see Fig. 29 (b)].

Thereafter, on the Ni thin film, formed was a
photoresist in the shape of an electrode 2 partly
overlapping with the electrode 1 at the middle of the
25 substrate. In the shape of this photoresist, the
electrode material 2c and insulating layer 5 were

1 etched, followed by peeling of the resist to form the
electrode 2 and an electrode spacing 6. The size
other than thickness, of each material, was made to be
the same as in Example 16.

5 Electron emission characteristics of the
electron-emitting device obtained according to the
above process were measured. As a result, there was
obtained the same electron emission as in Example 16.

Example 18

10 Example 16 was repeated except that the
material for fine particles and the organic solvent
comprising the organic metal compound were replaced by
a SiO_2 liquid coating preparation in which SnO_2 fine
particles of about 100 angstroms in primary particle
15 diameter were dispersed, to carry out an experiment.
As a result, there was obtained the same electron
emission as in Example 16.

Example 19

 An electron-emitting device was obtained
20 according to the previously described preparation
steps (a) to (d) of Fig. 30.

 More specifically, on a clean, quartz glass
substrate of about 1 mm thick, a SiO_2 liquid coating
preparation (Catapaste CCP, available from Okuno
25 Seiyaku Kogyo) was spin-coated with a spinner.

1 Thereafter the coating was baked for 1 hour at about
400°C to obtain an insulating layer 5a comprised of
SiO₂ and having a film thickness of about 1,000
angstroms. Subsequently, on the insulating layer 5a,
5 an organic solvent (Catapaste CCP, available from
Okuno Seiyaku Kogyo) containing an organic palladium
compound was spin coated with a spinner. Thereafter
the coating was baked for 10 minutes at about 250°C to
obtain fine particles 9 comprised of Pd in the state
10 that they are dispersed on the surface of the
insulating layer 5a [see Fig. 30 (a)].

Next, on the fine particles 9 and insulating
layer 5a, an insulating layer 5b comprised of SiO₂ was
coated in the same manner as the insulating layer 5a
15 to have a film thickness of about 500 angstroms,
followed by baking [see Fig. 30 (b)].

Thereafter, the insulating layers 5a and 5b
were etched using an aqueous hydrofluoric acid
solution by photolithoetching to form a stepped
20 portion of about 1,500 angstroms high at the middle of
the substrate 4 [see Fig. 30 (c)].

Ni electrodes 1 and 2 of about 5,000 angstroms
in film thickness was further formed by deposition
utilizing EB vacuum deposition in the manner that the
25 stepped portion may not be completely covered. A
space thus formed is designated as electrode spacing 6

1 [see Fig. 30 (d)].

Electron emission characteristics of the electron-emitting device obtained according to the above process were measured to have revealed that
5 there was obtained electron emission of, approximately, emitted electric current $I_e = 2.0 \mu A$ and emission efficiency $\alpha = 8 \times 10^{-3}$.

Example 20

As illustrated in Fig. 32, a Ni electrode 1 of
10 500 angstroms thick was formed on a glass substrate 4 by vacuum deposition. On the electrode 1, an insulating layer 5a made of SiO_2 was formed by vacuum deposition utilizing sputtering to have a film thickness of 1,000 angstroms.

15 Next, an electron-emitting layer made of Au was formed in 500 angstroms thickness by vacuum deposition (a layer 3a), and thereafter an insulating layer 5b (SiO_2) was formed with a film thickness of 1,000 angstroms by sputtering.

20 After the respective layers of the insulating layer 5a, electron-emitting layer 3a and insulating layer 5b were laminated, they are partly laminated on the electrode 1 as illustrated in Fig. 32 (a) along the pattern of the electrode 1, followed by
25 patterning. Next, an electrode 2 is laminated. The electrode 2 was made of Ni to make wiring resistance

1 lower. The thickness thereof was controlled to 5,000
angstroms to obtain necessary wiring resistance.

After the electrode 2 was laminated by vacuum
deposition, the electrode 2 was subjected to
5 patterning by, for example, usual photolithographic
process along the patterns of the electrode 1,
insulating layer 5a, electron-emitting layer 3a and
insulating layer 5b as illustrated in Fig. 32 (b).

A Pd organic metal solution (Catapaste,
10 available from Okuno Seiyaku Kogyo Co.) was spin
coated as an electron-emitting layer, followed by
baking for 10 minutes at 250°C to provide electron-
emitting bodies on the surface of a side wall of the
insulating layers. A voltage of 14 V was applied
15 between the electrodes 2a and 2b using a lead-out
electrode (not shown) provided above the device
substrate, and a lead-out voltage of 500 V was applied
to obtain emission of electron beams of 1.7 μ A.

Example 21

20 Fig. 33 (d) illustrate a cross section of a
electron-emitting device obtained in the present
Example [See Fig. 33 (a) to (d) as to the preparation
steps].

On a clean, quartz glass substrate 4 of about
25 1 mm thick, a solution prepared by mixing an organic
palladium compound solution (Catapaste CCP, available

1 from Okuno Seiyaku Kogyo) with a SiO_2 liquid coating
preparation (OCD, available from Tokyo Ohka Kogyo) to
have a molar ratio of SiO_2 : Pd of about 10 : 1 was
spin coated with a spinner. Thereafter the resulting
5 coating was baked for 1 hour at about 400°C to obtain
a SiO_2 insulating layer 5 having a film thickness of
about 3,500 angstroms and containing electron-emitting
materials 9 (Pd fine particles) [see Fig. 33 (a)].

Next, the insulating layer 5 was etched by
10 photolithoetching with use of an aqueous hydrofluoric
acid solution to form a stepped portion 18 of about
3,500 angstroms high at the middle of the substrate 4
[see Fig. 33 (b)].

Thereafter, Ni electrodes 1 and 2 of about 500
15 angstroms in film thickness was formed by deposition
utilizing EB vacuum deposition to have the shape
illustrated in Fig. 33 (c) in the manner that the
stepped portion may not be completely covered.

Electron emitting bodies 3b were further
20 provided on the surface of a side wall of the
insulating layer in the same manner as in Example 19
[see Fig. 33 (d)].

Electron emission characteristics of the
electron-emitting device obtained according to the
25 above process were measured to have revealed that
there was obtained electron emission of,

1 approximately, emitted electric current $I_e = 4 \mu\text{A}$ and
emission efficiency $\alpha = 2 \times 10^{-3}$, under applied device
voltage $V_f = 14 \text{ V}$ and lead-out voltage $V_a = 1 \text{ kV}$.

Example 22

5 Example 21 was repeated except that the
organic metal compound solution that formed the
electron-emitting bodies 3b in Example 21 was replaced
by a SiO_2 liquid coating preparation in which SiO_2
fine particles of about 100 angstroms in particle
10 diameter were dispersed, to form a similar electron-
emitting device. There were obtained substantially
the same results as in Example 21.

Example 23

Similar results were obtained also when the
15 organic metal compound solution employed to form the
electron-emitting bodies 3b in Example 20 was replaced
by a coating preparation in which SnO_2 fine particles
of about 100 angstroms in particle diameter were
dissolved by dispersion together with an organic
20 binder.

Example 24

On a substrate a SiO_2 film is vacuum deposited
to form an insulating layer 5a, on which Pd is vacuum
deposited in a thickness of 500 angstroms (electron-
25 emitting layer 3a) and further an insulating layer 5b

1 is formed by vacuum deposition of a SiO_2 film [see Fig. 34 (a)].

Next, the insulating layers 5a, 5b and electron-emitting layer 3a are etched to form a stepped portion 18 [see Fig. 34 (b)].

Thereafter, Ni is applied by masking vacuum deposition in a thickness of 500 angstroms to form electrodes 1 and 2 [see Fig. 34 (c)].

An organic palladium solution is further coated on the surface of the device substrate, followed by baking to provide electron-emitting bodies 3b on the sidewall of the stepped portion [see Fig. 34 (d)].

The resulting electron-emitting device has the structure that electron-emitting materials are present only in the vicinity of the stepped portion in contrast with Example 20.

Good results were obtained as in Example 20.

Example 25

Example 24 was repeated to obtain an electron-emitting device, except that the Pd fine particles film of the electron-emitting layer 3a in Example 24 was replaced by a layer obtained by coating a Pd fine particles dispersed solution as shown in Fig. 35.

There was obtained the same electron emission.

Example 26

1 The same electron emission as in Example 20
was obtained also in a device in which as illustrated
in Fig. 36 a Pd vapor-deposited film serving as an
electron-emitting layer 3a was disposed in an
5 insulating layer 5 containing electron-emitting
materials 9 as Pd fine particles, a stepped portion
was formed, and electron-emitting bodies 3b were
further provided on the sidewall of the stepped
portion by coating an organic palladium solution
10 followed by baking.

Example 27

In the constitution illustrated in Fig. 37, on
a glass substrate 4, titanium electrodes 1 and 2 were
formed with a thickness of 1,000 angstroms, $L = 0.8 \mu m$
15 and $W = 300 \mu m$, and thereafter SnO_2 and Pd were
arranged as fine particles in a dispersed state
between the electrodes.

As a method therefor, a SnO_2 dispersion (SnO_2 :
1g; solvent: MEK (methyl ethyl ketone)/cyclohexanone =
20 3/1, 1,000 cc; butyral: 1 g) having a primary particle
diameter of 80 to 200 angstroms was spin-coated,
followed by heating. A Pd dispersion having a primary
particle diameter of about 100 angstroms was further
spin coated, followed by heating to obtain an electron-
25 emitting device.

A voltage of about 10^{-5} Torr was applied

1 between the electrodes of the device thus formed. As
a result, there was obtained an electron emission
current of 1.1 μA under an applied voltage of 15 V.

Thus, substantially the same electron emission
5 is obtained even under the applied voltage of lower by
approximately 5 volts than that of the device
containing no Pd fine particles and solely comprised
of SnO_2 . In this manner, the drive voltage was able
to be lowered by the device containing different kind
10 of fine particles.

Example 28

In regard to the SnO_2 dispersion of Example
27, a dispersion of SnO_2 of 80 to 200 angstroms in
particle diameter and a dispersion of SnO_2 of about
15 3,000 angstroms in particle diameter were prepared,
and two kinds of the SnO_2 dispersions were coated in
the same manner as in Example 27 but in one step for
each dispersion, thus arranging fine particles in a
dispersed state to obtain a electron-emitting device.

20 As electron emission characteristics of the
device thus formed, there was obtained an electron
emission current of about 1.1 μA under an applied
voltage of 17 V.

Thus, substantially the same electron emission
25 is obtained even under the applied voltage of as about
3 V lower than that of the device obtained by coating

1 in two steps the dispersions of SnO_2 of 80 to 200
angstroms in particle diameter. In this manner, the
drive voltage was able to be lowered by adding the
particles having a larger particle diameter.

Sub-B 5 [Effect of the invention]

As described above, according to the electron-
emitting device of the present invention and the
method for preparing the same, electron-emitting
devices that can have stable structure even if the
10 electrode spacing having the electron-emitting
materials is made very narrow can be formed without
applying the forming required in the prior art.

Accordingly, the electron-emitting devices
prepared by the present invention are quite free from
15 the difficulties conventionally accompanying the
forming treatment, so that it becomes possible to
manufacture the devices having less irregularities in
characteristics, in a large number and with ease,
bringing about great industrial utility.

20 The electron-emitting device obtained by the
present invention can also be utilized in planar
display devices in which the electron-emitting devices
are mounted in a single plane and electrons emitted by
applying a voltage are accelerated to stimulate
25 phosphors to effect light-emission.

An electron-emitting device that is stabler

1 and of longer life and also has a good efficiency can
also be obtained by bringing the electrode
constitution into a multi-layer constitution.

Also, the electron-emitting device in which
5 the fine particles are fixed in the insulating layer
is free of any movement of the fine particles during
drive, and thus can be an electron-emitting device
that is stable and of elongated life.

The electron emission efficiency can be
10 improved by suitably adjusting the density of the fine
particles.

The electron-emitting device having the
semiconductor layer as illustrated in Fig. 17 makes it
possible to lower the drive voltage by controlling the
15 electrical resistance of the semiconductor, and also
can be effective in improvement of emitted currents.

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